Cu K-edge XAFS in CdTe before and after treatment with CdCl$_2$

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ABSTRACT

We have used the fine structure in the Cu K-edge x-ray absorption spectrum to help elucidate the lattice location of Cu in polycrystalline, thin-film CdTe solar cells. In particular, we have studied how the typical CdCl$_2$ vapor treatment in dry air changes the local environment of the Cu in CdTe. We find the Cu absorption spectrum to be similar to that of Cu$_2$Te in the as-deposited CdTe film but to convert to a spectrum similar to Cu$_2$O environment after the vapor CdCl$_2$ treatment.

INTRODUCTION

High performance CdS/CdTe thin film solar cells are usually completed with a low resistance Cu back contact. The copper appears to be critical for achieving heavy p-type doping of the CdTe at the contact. It is also known that Cu doping can increase the open-circuit voltage. However, copper is also a fast diffuser, [1] which can accumulate at CdS/CdTe junction and is suspected of playing a role in cell performance deterioration under certain conditions.

High-temperature CdCl$_2$ treatment in the presence of oxygen is a critical step needed to improve the performance of CdTe thin-film cells, which can improve the cell efficiency a factor of two or more. [2,3] However the process is not well understood yet. Thus, for this study, samples were prepared through the same processes as completed cells except that the transparent conducting oxide (TCO) and CdS layers were omitted.

X-ray absorption fine structure (XAFS) is a powerful technique in materials science research for understanding the lattice environment around designated element atoms, which include two independent parts: the x-ray absorption near edge structure (XANES) and the extended x-ray absorption fine structure (EXAFS). The XANES is the absorption fine structure spectrum covering the range between the absorption edge of the element itself and the point usually considered to be 50 eV beyond the threshold. The EXAFS is the periodic oscillatory structure in the absorption spectrum above the edge due to the phase difference between back-scattered and out-going electron waves. The lattice environments are derivable from absorbance spectra by mathematically converting the EXAFS spectrum into a radial distribution function (RDF).

EXPERIMENTAL DETAILS

The 2-3 micron CdTe layers were magnetron sputtered at ~ 250 °C, as described in paper B3.7 of this proceeding, onto either fused silica or Kapton polyimide sheet (from DuPont High Performance Materials) substrates [4]. All the samples were prepared with 40 ~ 200 Å

evaporated Cu layers. Diffusion in N_2 at 150 or 200 $^\circ$C for at least 45 minutes is applied to all samples. Short 5% hydrochloric acid etchings are also applied to remove the metallic copper left on the film surface. (We found that the x-ray fluorescence from a film with a 200 Å deposited and diffused Cu layer, typically dropped a factor of two after etching. Thus we estimate that about 100Å of Cu diffused into a 3 μm film. This would imply that the average Cu concentration in a typical film is about 0.3 %.) Some of the samples were annealed at 385 $^\circ$C in $CdCl_2$ vapor in a dry air environment for 30 minutes, before Cu deposition, diffusion and etching. These samples are compared to the non-chloride treated samples in Cu K-edge XAFS (X-ray Absorption Fine Structure).

Data were obtained at the Materials Research Collaborative Access Team (MR-CAT) beam-line at the Advanced Photon Source (Argonne IL) with the system shown in Fig. 1. The Cu K-edge x-ray absorption spectra of the Cu-doped CdTe samples were collected in fluorescence geometry with a 13-element high purity Ge detector, by setting a 600 eV wide window at the position of Cu K_α (8048 eV) in the fluorescence spectrum (Fig. 2), since the copper fluorescence intensity is proportional to the absorbance by copper in the thin films. Reference samples of CuO, Cu_2O, $CuCl_2$ and Cu_2Te powders were applied to the adhesive of several layers of Kapton tapes and the absorption spectra were collected in the transmission geometry with detection by the N_2 ion chamber (Transmitted Intensity Monitor).
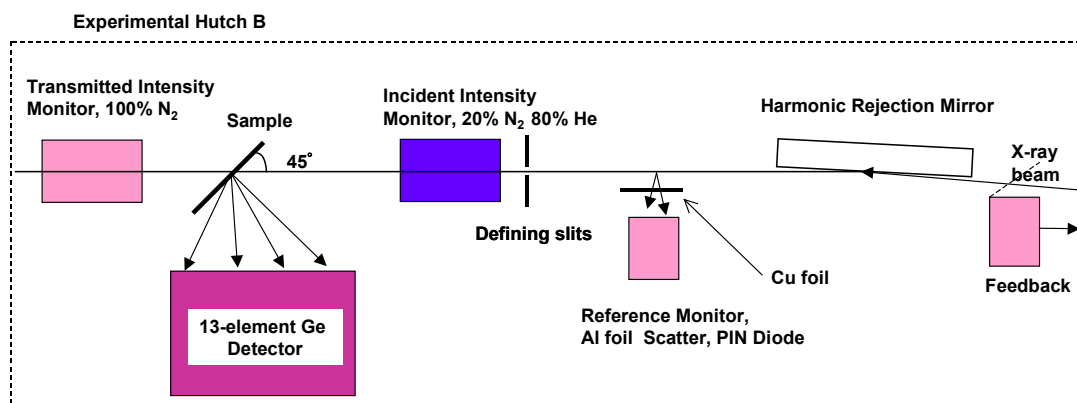
Figure 1. Experimental setup at MR-CAT
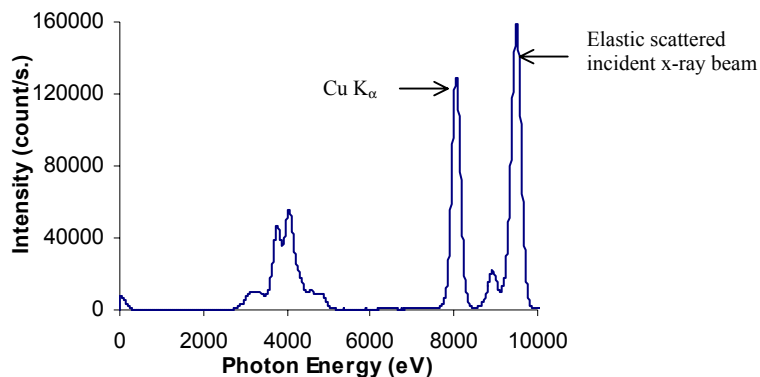
Figure 2. X-ray fluorescence spectrum of a Cu-diffused CdTe film excited by
9.5 keV x-ray beam, collected by the 13-element Ge detector

DISCUSSION

<u>Global view of Cu K-edge XAFS</u>

The computed absorption coefficient for a modeled CdTe film with 20 % Cu is plotted in Fig. 3. The actual attenuation coefficient μ of 8.8, 9.5, and 10.0 keV x-ray photons were directly measured to be 0.15, 0.12, and 0.10 μm^{-1} by transmission through a series of sputtered CdTe films on polyimide tape, agreeing with the computed μ value. Note that our film thicknesses were less than the absorption length. The photon energy range from 8.8 to 10 keV is the same as the one for which XAFS data are collected. Fused silica and polyimide tape were selected to avoid residual heavy elements, such as copper from the soda-lime glass, which might overlap the Cu signal from the CdTe films.
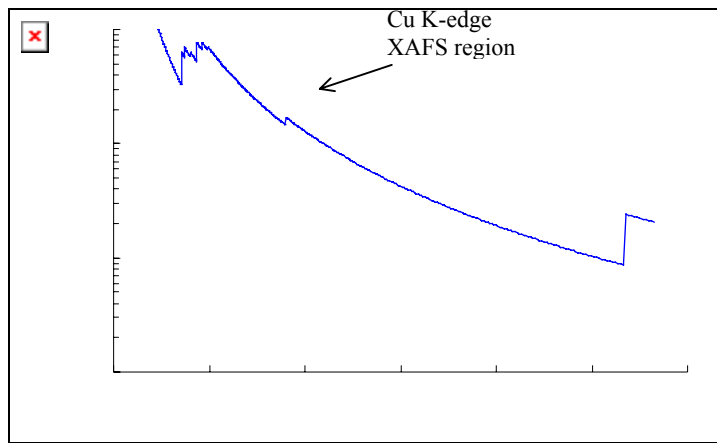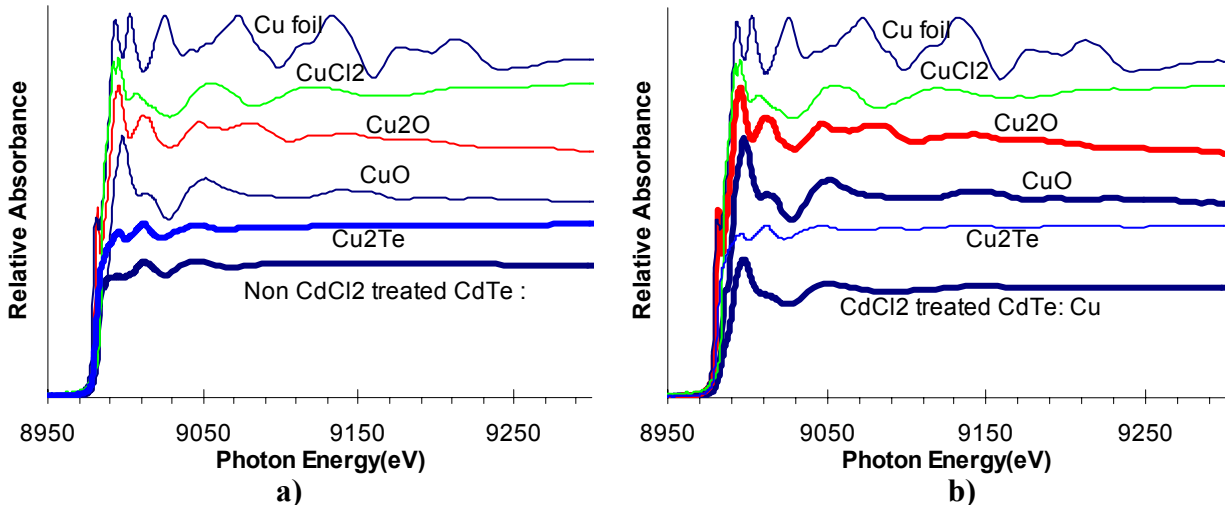

Figure 3. Computed x-ray absorption coefficient spectrum of CdTe with 20% Cu [5]

<u>Comparison of XANES spectra</u>

Figure 4. X-ray Absorption Near Edge Structure (XANES) spectra. a) Non-chloride treated CdTe films with diffused copper show features similar to Cu_2Te; b) chloride-treated CdTe films with diffused copper show features similar to Cu_2O and CuO

As shown in Fig. 4, comparison with reference materials in the XANES region usually helps to understand the predominant chemical bonds surrounding the core atoms in unknown samples. Before $CdCl_2$ treatment all of the CdTe films are observed to have features similar to Cu_2Te (see Fig 4a). However, the films with $CdCl_2$ treatment show features most similar to Cu_2O and CuO (see Fig. 4b). Note that the absorption amplitude depends on the sample thickness in direct transmission measurements and depends on detector efficiency and sample thickness for the CdTe: Cu films when fluorescence detection was used. For convenience of comparison, absorption curves in relative magnitude are plotted in Fig. 4.

Data Analysis

EXAFS can be extracted from the x-ray absorption spectra by removing the background. The x-ray absorption backgrounds are calculated as x-ray absorbance in the sample without the electron scattering contribution. Finally the Fourier transform of this fine structure vs. k is the radial distribution function of EXAFS. [6] Our analyses were performed through IFEFFIT an interactive program for XAFS analysis. [7]

a)   b)
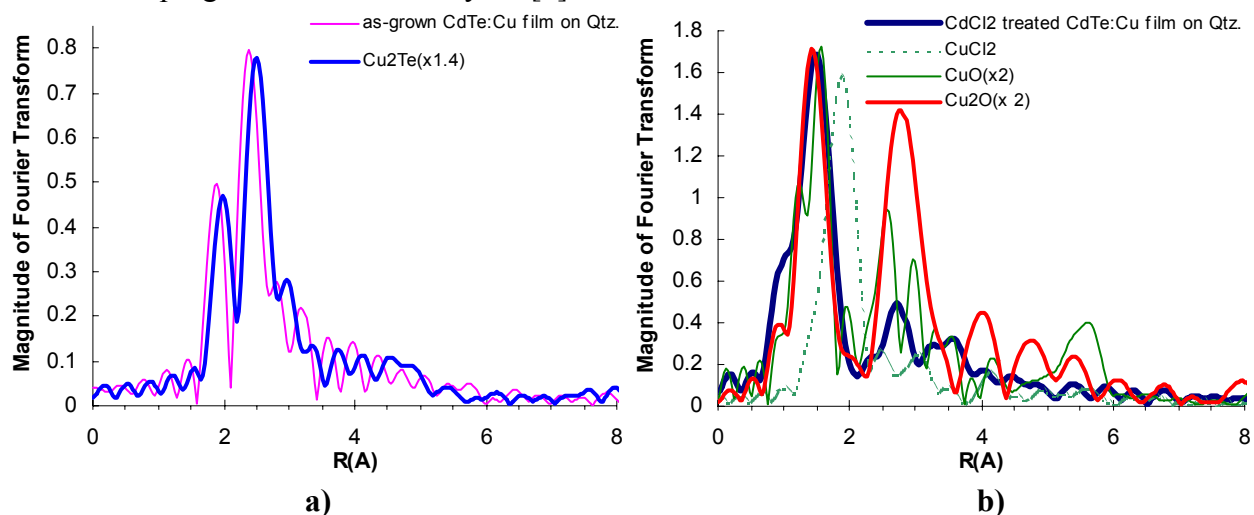
Figure 5. Radial Distribution Function after Fourier Transform

The radial distribution functions for the two cases--without $CdCl_2$ treatment and with $CdCl_2$--are shown in Fig 5. In the RDF of Fig. 5a, we also observe that the peak of the first nearest neighbor at 2.42 Å shifts to shorter distance about 0.1 Å than the one in cuprous telluride, but otherwise there is a strong correspondence. We are still studying the data and analysis to determine whether this shift is real. The magnitude in FT mostly depends on the coordination number in the neighbor shell. Without further theoretical modeling, we are not able to fully interpret the difference of the FT magnitudes of various peaks.

For the $CdCl_2$ treated films, the shape of the RDF and the position of the peaks are substantially changed. Thus, we infer that the chemical environment of the typical copper atom is substantially changed. The peak of the first nearest neighbor resides at a position neither the same as cuprous telluride, Cu_2Te, nor cupric chloride, $CuCl_2$, but corresponds closely to cuprous oxide, Cu_2O at 1.50 Å, as shown in Fig. 5b. Although the XANES spectra (Fig. 4b) show features similar to CuO in the Cl-treated film, the RDF does not prove the existence of CuO in the film. Since the second nearest neighbors of copper in cuprous oxide are copper atoms, [8] the

fact that the second nearest neighbor peaks in Fig. 5b, are very different suggests that we are not seeing nanocrystal inclusions of cuprous oxide but rather copper-oxygen clusters formed in the film or quite likely along the grain boundaries.

Discussion

Our films were diffused with a typical concentration of copper of about 0.3% or an average density of 1-2 x 10^{20} cm^{-3}. However, capacitance-voltage (C-V) measurements on typical CdTe solar cells, including our sputtered cells indicate a typical doping concentration of holes of a few times 10^{14} cm^{-3}. [9] Secondary ion mass spectroscopy (SIMS) on some CdTe cells has shown Cu atomic concentrations of a few times 10^{19} cm^{-3}. [10] Our preparation of films was done with evaporated Cu amounts only slightly higher than we use for cell fabrication. Clearly much Cu is not active as an acceptor in these films and there is considerable interest in where the non-electrically active Cu is located. Based on our x-ray absorption fine structure measurements, we conclude that the answer depends entirely on whether the film has received the typical treatment with CdCl$_2$. Thus, films which received the Cu diffusion having no prior treatment with CdCl$_2$ appear to show the Cu mostly bound with Te similar to Cu$_2$Te. *However*, if the film had received the CdCl$_2$ treatment, *which for cells is always done in the presence of some O$_2$*, then the Cu appears to be bound not with Cl but with O. The most plausible interpretation is that most of the copper was available at grain boundaries where it could easily be oxidized during the CdCl$_2$ treatment. Note that it is generally understood that this CdCl$_2$ treatment is important for passivating the grain boundaries and thus is a critically important step in the fabrication of high efficiency polycrystalline thin-film solar cells. These x-ray absorption fine structure measurements point toward a plausible interpretation of this chloride treatment as well as other observations that the preparation of a Te-rich surface (e.g., by chemical etching with Br$_2$/methanol or HNO$_3$/H$_3$PO$_4$ [11]) is often important for fabricating high efficiency cells. (See Paper B3.1 in these Proceedings.) The wider band-gap cuprous oxide on the CdTe grain boundaries may prevent the recombination of electron-hole pairs there. [12] However, more information on band lineups between Cu$_2$O and CdTe will be needed to confirm that this is a plausible interpretation.

Fitting to theoretical standards derived from the *ab initio* multiple-scattering code FEFF [13] is in progress to obtain more detailed information about the near-neighbor distance and the coordination numbers of the environment surrounding the copper atoms.

ACKNOWLEDGEMENTS

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